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PERMANENT MAGNET AND MANUFACTURING METHOD THEREOF

Koichiro Tsuji et la.

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PERMANENT MAGNET AND MANUFACTURING METHOD THEREOF  
[Eikyujishaku oyobi sono seizohoho]

Inventors:	Koichiro Tsuji, et al.
Applicant:	Yasaki Sogyo K.K.

[Attached amendments have been incorporated into the text of the translation.]

Claims

1. A permanent magnet characterized by the fact that an organic modified silica film is formed on the surface of a Nd-Fe-B type alloy magnet.
2. The permanent magnet described in Claim 1 characterized by the fact that the thickness of the organic modified silica film is in the range of 0.1-500  $\mu\text{m}$ .
3. The permanent magnet described in Claim 1 or 2 characterized by the fact that the organic modified silica film is comprised of a silica precursor and at least one organic precursor selected from methacrylate type precursors, epoxy type precursors, and vinyl type precursors.
4. The permanent magnet described in Claim 1, 2, or 3 characterized by the fact that the organic modified silica film is comprised of 30-70 mol% of a silica precursor component and 30-70 mol% of an organic precursor component.

5. The permanent magnet described in Claim 1, 2, 3, or 4 characterized by the fact that the organic modified silica film is a silica-methacrylate type cured film.

6. A permanent magnet manufacturing method characterized by the following facts: acidic water is added and stirred with a mixture consisting of a silica precursor and at least an organic precursor selected from methacrylate type precursors, epoxy type precursors, and vinyl type precursors to form a sol as a result of hydrolysis and co-condensation; after a Nd-Fe-B type alloy magnet is immersed in the obtained sol and then pulled up, a curing treatment is carried out under heating to form an organic modified silica film on the surface of the aforementioned Nd-Fe-B type alloy magnet.

7. The permanent magnet manufacturing method described in Claim characterized by the fact that 6 the thickness of the formed organic modified silica film is adjusted to 0.1-500  $\mu\text{m}$  by controlling the concentration of the sol and the speed of pulling up the Nd-Fe-B type alloy magnet.

8. The permanent magnet manufacturing method described in Claim 6 or 7 characterized by the fact that the sol is formed using a mixture consisting of 30-70 mol% of the silica precursor component and 30-70 mol% of the organic precursor component.

9. The permanent magnet manufacturing method described in Claim 6, 7, or 8 characterized by the fact that the sol is formed from a mixture consisting of a silica precursor component and an organic methacrylate precursor component.

10. The permanent magnet manufacturing method described in Claim 6, 7, 8, or 9 characterized by the fact that moisture is removed from the aforementioned sol film by means of IR irradiation or vacuum heating before performing the thermal curing treatment on the sol film formed on the surface of the Nd-Fe-B type alloy magnet.

11. The permanent magnet manufacturing method described in Claim 6, 7, 8, 9, or 10 characterized by the fact that the sol contains 2-40 mol% of at least one type of solid powder selected from zinc chromate, iron oxide, mica, silica, titanium oxide, and zirconia in addition to the mixture of the silica precursor component and the organic precursor component.

#### Detailed explanation of the invention

[0001]

#### Industrial application field

The present invention pertains to a type of permanent magnet and its manufacturing method. More specifically, the present invention pertains to a type of permanent magnet with excellent magnetic characteristics and corrosion resistance and to a method that can manufacture the aforementioned permanent magnet efficiently at low cost.

[0002]

Prior art

Since rare earth iron sintered alloy magnet, especially, Nd (niobium) – Fe (iron) – B (boron) alloy magnet has excellent magnetic characteristics and low cost, it has been widely used in the field of OA equipment and precise equipment, etc.

[0003]

However, since the Nd-Fe-B type alloy magnet is mainly composed of iron, it will be easily affected by the moisture or oxygen in the air to become rusty. The corrosion resistance is poor, and the service life is short. That is its greatest disadvantage.

[0004]

Conventionally, in order to block penetration of moisture, etc. from the surface of Nd-Fe-B type alloy magnet to improve the corrosion resistance of that alloy magnet, the method of coating an organic resin, such as an epoxy resin, on the surface of the aforementioned alloy magnet and the method of plating an anticorrosion metal film made of nickel, etc. have been used. In this methods, however, the adhesion between the aforementioned alloy magnet and the aforementioned coated film or plated film is poor, and the mechanical strength is deteriorated. As a result, the performance of the magnet cannot be well improved.

[0005]

Based on this fact, many methods have been proposed in recent years in order to adjust and improve the corrosion resistance and mechanical properties of Nd-Fe-B type alloy magnet. For example, (1) linseed oil, wax, varnish, water glass, polyester resin, phenol resin, epoxy resin, or other sealing agent is filled in the spaces between the crystal particles of the aforementioned alloy magnet, and a surface treatment, such as coating, is performed on the surface of the magnet in order to improve the corrosion resistance (Japanese Kokai Patent Application No. Sho 62[1987]—287004). (2) After organic titanium is attached to the surface of the aforementioned alloy magnet, a heat treatment is carried out in an inactive gas in order to improve the corrosion resistance (Japanese Kokai Patent Application No. Sho 63[1988]-168009). (3) A silicon film made of water glass, etc. is formed on the surface of the alloy powder used as the material of the aforementioned alloy magnet. Then, the alloy powder is used to mold the magnet. In this way, generation of coarse crystal particles can be prevented, and the process can be simplified. This method can be used in an atmosphere with a high oxygen partial pressure (Japanese Kokai Patent Application No. Hei 3[1991]-295204).

[0006]

For the Nd-Fe-B type alloy magnet manufactured using the aforementioned methods, although the mechanical property can be well improved, the improvement over the corrosion resistance is still insufficient. In particular, in said methods (1) and (3), large-scale equipment is required, which complicates the process. As a result, the cost of the magnet cannot be lowered.

[0007]

Problems to be solved by the invention

The purpose of the present invention is to solve the problems of the aforementioned conventional permanent magnet.

[0008]

Consequently, the purpose of the present invention is to provide a type of permanent magnet with excellent magnetic characteristics and corrosion resistance and provide a method that can manufacture the aforementioned permanent magnet efficiently at low cost.

[0009]

In order to realize the aforementioned purpose, the present invention provides a permanent magnet characterized by the fact that an organic modified silica film is formed on the surface of a Nd-Fe-B alloy magnet.

[0010]

The present invention also provides a permanent magnet manufacturing method characterized by the following facts: acidic water is added and stirred with a mixture consisting of a silica precursor and at least an organic precursor selected from methacrylate precursors, epoxy precursors, and vinyl precursors to form a sol as a result of hydrolysis and co-condensation; after a Nd-Fe-B alloy magnet is immersed in the obtained sol and then pulled up, a curing treatment is carried out under heating to form an organic modified silica film on the surface of the aforementioned Nd-Fe-B alloy magnet.

[0011]

Operation

Since an organic modified silica film is formed on the surface of the Nd-Fe-B magnet for the permanent magnet of the present invention, while it is able to maintain the excellent magnetic characteristics of the Nd-Fe-B alloy magnet, penetration of moisture or oxygen can be well

protected by the organic modified silica film so that excellent corrosion resistance can be displayed, and long service life of magnet can be realized.

[0012]

Also, by using the permanent magnet manufacturing method disclosed in the present invention, permanent magnet with excellent magnetic characteristics and corrosion resistance can be manufactured efficiently at low cost by a simple process, which thermally cures magnet after dipping it in a sol without requiring the coating, plating, or other tedious operation in the conventional technology.

[0013]

#### Application examples

In the following, the application examples of the permanent magnet and its manufacturing method disclosed in the present invention will be explained in more detail with reference to figures.

[0014]

Figure 1 is a cross-sectional view illustrating an example of the permanent magnet disclosed in the present invention. Figure 2 is a schematic diagram illustrating the permanent magnet manufacturing method disclosed in the present invention.

[0015]

In the application example shown in Figure 1, permanent magnet 1 disclosed in the present invention is comprised of Nd-Fe-B alloy magnet 2 and organic modified silica film 3 formed on its surface.

[0016]

Said Nd-Fe-B alloy magnet 2 used in the present invention refers to a magnet that contains at least niobium, iron, and boron. In addition to these components, if necessary, it may also contain a small amount of rare earth elements selected from lanthanum, cerium, praseodymium, dysprosium, holmium, and terbium, metal elements selected from aluminum, titanium, vanadium, chromium, manganese, cobalt, nickel, zirconium, niobium, molybdenum, tantalum, and tungsten.

[0017]

For the proportion of each component in the Nd-Fe-B alloy magnet, the content of niobium is preferred to be in the range of 5-15 mol%, the content of iron is preferred to be in the range of 70-90 mol%, and the content of boron is preferred to be in the range of 2-10 mol%.

[0018]

Nd-Fe-B alloy magnet 2 can be manufactured using the conventional method. For example, a raw material consisting niobium, iron, boron, and other metals in prescribed proportions is prepared. The mixture is cast in high vacuum by means of high-frequency heating. The obtained ingot is pulverized and roughly powdered to obtain an alloy powder. Then, the aforementioned alloy powder is finely powdered using a jet mill, etc. The micropowder is molded in a magnetic field. The obtained molding is sintered at a high temperature in high vacuum in a sintering furnace. In this way, the desired Nd-Fe-B alloy magnet can be obtained.

[0019]

Organic modified silica film 3 is a curing film formed from a silica precursor and at least one organic precursor selected from methacrylate precursors, epoxy precursors, and vinyl precursors, preferably, a methacrylate precursor. The film thickness is in the range of 0.1-500  $\mu\text{m}$ , preferably, in the range of 0.1-50  $\mu\text{m}$ .

[0020]

It is particularly preferred that said organic modified silica film 3 be a cured film comprised of 30-70 mol% of the aforementioned silica precursor component and 30-70 mol% of the aforementioned organic precursor component.

[0021]

In this case, tetraethyl ortho silicate is used as the aforementioned silica precursor component.

[0022]

Examples of the methacrylate precursors that can be used for the aforementioned organic precursor component include organo modified alkoxide, 3-methacryl hydroxypyrrutrimethoxysilane (MPMS), etc. An example of the epoxy precursor is 3-glycyloxypropyl trimethoxysilane (GPMS). An example of the vinyl precursor is vinyl-trimethoxysilane (VES).

[0023]

The permanent magnet of the present invention having an organic modified silica film formed on the surface of a Nd-Fe-B alloy magnet maintains the excellent magnetic characteristics of the Nd-Fe-B alloy magnet and can well prevent penetration of moisture or oxygen by the organic modified silica film so that excellent corrosion resistance can be displayed, and a long service life of the magnet can be realized. The permanent magnet of the present invention is very useful in the field of OA equipment and precise equipment.

[0024]

In the following, a detailed example of the permanent magnet manufacturing method disclosed in the present invention will be explained with reference to Figure 2.

[0025]

In the manufacturing method of the present invention, the sol-gel method that can easily deposit film is used to form said organic modified silica film 3.

[0026]

A sol consisting of a silica precursor and an organic precursor can be prepared easily as follows. A mixture prepared by mixing a silica precursor and an organic precursor in prescribed proportions is used as the Ormosil [Transliteration] for forming the sol. Acidic water of hydrochloric acid, nitric acid, or sulfuric acid is then added, followed by fully stirring to carry out hydrolysis and co-condensation to manufacture the aforementioned sol.

[0027]

In this case, when forming the sol, the ratio of the silica precursor component/organic precursor component is in the range of 30-70 mol%/30-70 mol%, preferably, in the range of 30-50- mol%/50-70 mol%. If the proportion of the silica precursor is less than 30 mol%, the sol will separate into two phases. If it is more 70 mol%, the sol will be gelled during a short period of time.

[0028]

Next, the obtained sol is added to any dip coating apparatus. After a Nd-Fe-B alloy magnet is dipped (dipping) in the sol for a prescribed period of time and is then pulled up, it is fed into an oven or other heat treatment apparatus, in which thermal curing is carried out at 100-200°C for 5-15 h. In this way, an organic modified silica film with uniform film thickness can be formed.



[0029]

It is preferred to adjust the thickness of the formed organic modified silica film to 0.1-500  $\mu\text{m}$  by properly controlling the concentration of the aforementioned sol and/or the speed of pulling up the Nd-Fe-B alloy magnet.

[0030]

Also, if the sol contains a lot of water, it is preferred to remove the water from the sol film by means of IR irradiation or vacuum heating before thermally curing the sol film formed on the surface of the Nd-Fe-B alloy magnet.

[0031]

The mechanical property of the organic modified silica film can be further improved by adding at least one type of solid powder selected from zinc chromate, iron oxide, mica, silica, titanium oxide, and zirconia in an amount of 2-40 mol% with respect to the sol comprised of the silica precursor component and the organic precursor component. In this case, after the solid powder is added into the sol, it is preferred to accelerate the dispersibility of the solid powder in the sol by conducting a supersonic treatment.

[0032]

By using the permanent magnet manufacturing method disclosed in the present invention, permanent magnet with excellent magnetic characteristics and corrosion resistance can be manufactured efficiently at low cost by a simple process, which thermally cures magnet after dipping it in a sol without requiring the coating, plating, or other tedious operation in the conventional technology.

[0033]

In the following, the constitution and the effect of the present invention will be explained in more detail based on an experimental example.

[0034]

#### Experimental example

##### (1) Preparation of Nd-Fe-B alloy magnet

A rectangular parallelepiped shaped Nd-Fe-B alloy magnet with sizes 3 mm x 10 mm x 50 mm comprised of 5-15 mol% niobium, 70-90 mol% of iron, and 2-10 mol% of boron was prepared.

[0035]

(2) Preparation of sol

13.44 mL of tetraethyl ortho silicate and 34.50 mL of organo modified alkoxide were mixed for 5 min. Then, 0.60 mL of 35% hydrochloric acid and 6.0 mL of water were added, followed by fully mixing. In 1 min since mixing was started, the mixture was transparent and generated heat quickly. After about 20 min of mixing, a transparent sol was obtained.

[0036]

(3) Dip coating

The aforementioned sol was added to a dip coating apparatus. The Nd-Fe-B alloy magnet installed on the holder was dipped in the sol and then pulled up at a velocity of 9 cm/min.

[0037]

(4) Thermal curing treatment

After the magnet was pulled up from the sol, curing of the organic modified silica film was started immediately. First, a vacuum heat treatment was carried out at 120°C for 3 h to evaporate the water. Then, a thermal curing treatment was carried out in a 160°C heating oven for 10 h. As a result, a cured silica-methacrylate film with a uniform thickness of 10  $\mu\text{m}$  was formed. This permanent magnet was used as sample A.

[0038]

For the purpose of comparison, a nickel film with a thickness of 10  $\mu\text{m}$  was plated using the conventional method on the surface of the same Nd-Fe-B alloy magnet. This permanent magnet was used as sample B.

[0039]

An epoxy resin film with a thickness of 20  $\mu\text{m}$  was coated using the conventional method on the surface of the same Nd-Fe-B alloy magnet. This permanent magnet was used as sample C.

[0040]

(4) Evaluation of corrosion resistance

An anticorrosion test was carried out under the following conditions to the three permanent magnets obtained above. The evaluation results are shown in Table 1.

[0041]

(1) Heat impact test

A process of room temperature – (5 min) → 40°C (kept for 1 h) – (5 min) → 120°C (kept for 1 h) – (5 min) → Room temperature was repeated for 500 cycles. The result was evaluated based on the following standards.

O No surface crack or corrosion at all

X No surface crack, but there is somewhat corrosion

[0042]

(2) High humidity test

A high humidity test was carried out at 80°C and humidity of 95% for 500 h. The result was evaluated based on the following standards.

O No surface crack or corrosion at all

Δ No surface crack, but there is a little corrosion

X Cracks occur over the entire surface, and there is also corroded area.

[0043]

(3) High temperature test

A high temperature test was carried out at 120°C for 1000 h. The result was evaluated based on the following standard.

O No surface crack or corrosion at all

[0044]

(4) Salt water spray test

A test was carried out using 5 wt% salt water under the conditions of 35°C and 48 h according to ASTM B-117. The result was evaluated based on the following standards.

O No surface crack or corrosion at all

X Cracks occur over the entire surface, and there is also corroded area.

[0045]

Table 1

①	サンプル名	A	B	C
②	熱衝撃試験	○	×	○
③	高湿度試験	○	△	×
④	高温腐食試験	○	○	○
⑤	塩水噴霧試験	○	×	×
⑥	総合評価	○	×	×

Key: 1 Sample No. 1  
 2 Heat impact test  
 3 High humidity test  
 4 High temperature test  
 5 Salt water spray test  
 6 General evaluation

As can be seen from the results shown in Table 1, compared with the conventional permanent magnet B or C, permanent magnet A of the present invention has excellent corrosion resistance.

[0046]

#### Effects of the invention

As explained above, since the permanent magnet of the present invention has an organic modified silica film formed on the surface of a Nd-Fe-B alloy magnet, the excellent magnetic characteristics of the Nd-Fe-B alloy magnet can be maintained, and penetration of moisture or oxygen can be well prevented by the organic modified silica film so that excellent corrosion resistance can be displayed, and a long service life of the magnet can be realized.

[0047]

Also, by using the permanent magnet manufacturing method disclosed in the present invention, permanent magnet with excellent magnetic characteristics and corrosion resistance can be manufactured efficiently at low cost by a simple process, which thermally cures magnet after dipping it in a sol without requiring the coating, plating, or other tedious operation in the conventional technology.

### Brief description of the figures

Figure 1 is a cross-sectional view illustrating an example of the permanent magnet disclosed in the present invention.

Figure 2 is a schematic diagram illustrating the permanent magnet manufacturing method disclosed in the present invention.

### Explanation of the symbols

- 1 Permanent magnet
- 2 Nd-Fe-B alloy magnet
- 3 Organic modified silica film

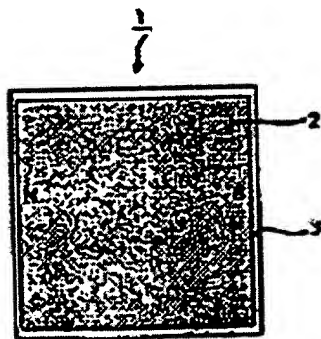


Figure 1

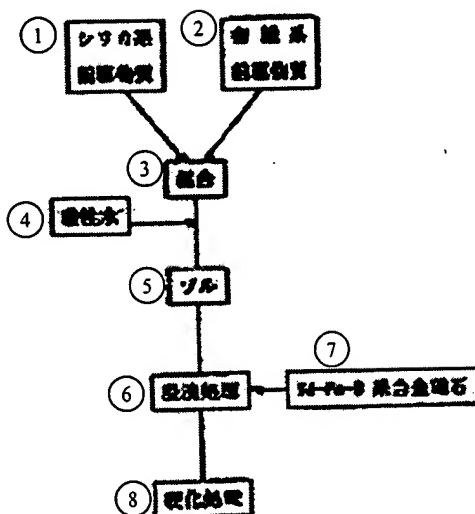


Figure 2

- Key:
- 1 Silica precursor
  - 2 Organic precursor

- 3 Mixing
- 4 Acidic water
- 5 Sol
- 6 Dipping treatment
- 7 Nd-Fe-B alloy magnet
- 8 Hardening treatment